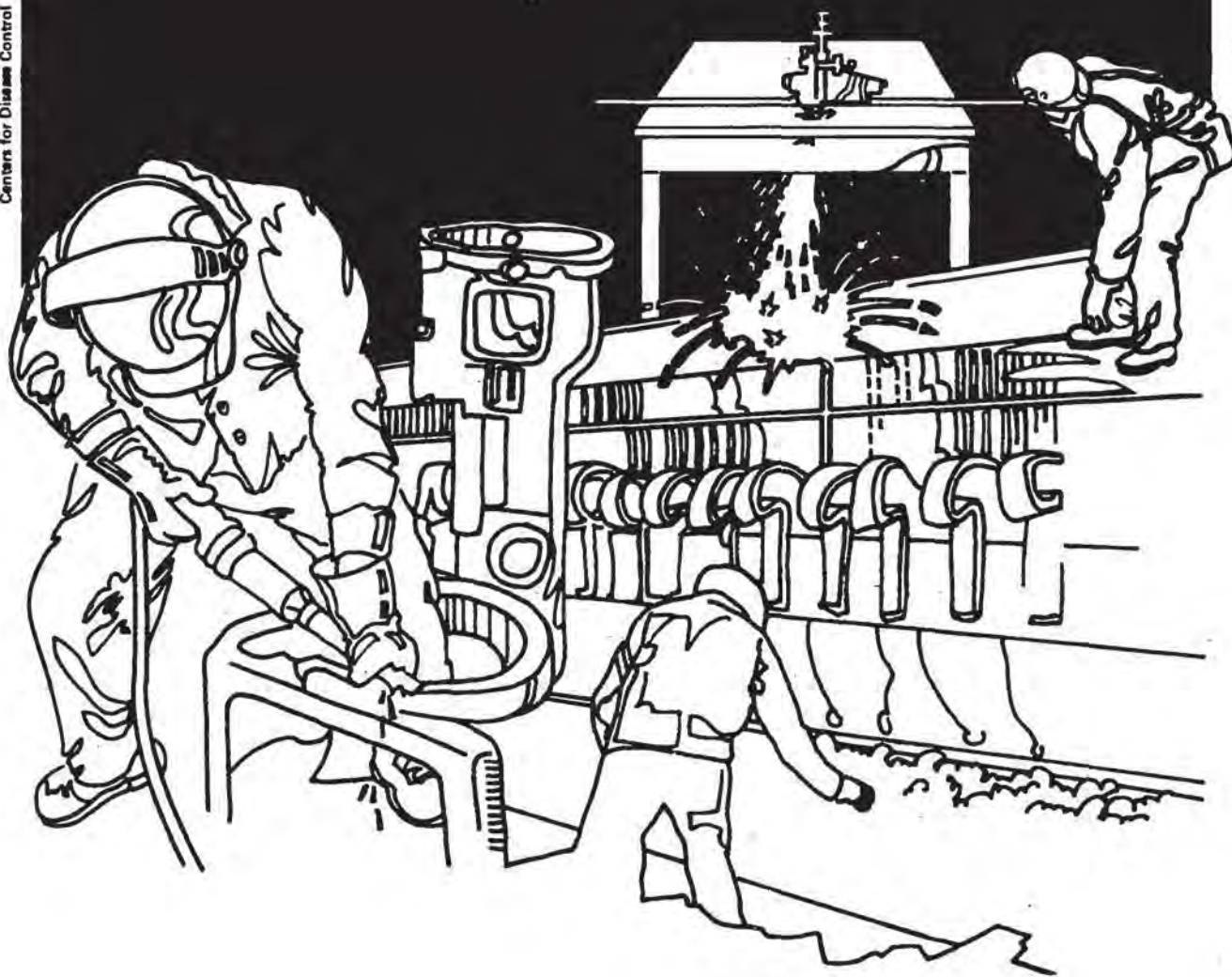


NIOSH



Health Hazard Evaluation Report

HETA 84-426-1963
ORMET CORPORATION
HANNIBAL, OHIO

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

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ORMET CORPORATION
HANNIBAL, OHIO

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I. SUMMARY

On July 6, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation from the Chairman of the Safety and Health Committee of Local 5724, United Steelworkers of America, to evaluate complaints of respiratory and skin irritation among potroom employees of the Ormet Corporation, Hannibal, Ohio.

Environmental monitoring of a cross-section of potroom employees at Ormet was conducted for determination of personal (breathing zone) exposures to fluorides, sulfur dioxide (SO_2), coal tar pitch volatiles (CTPVs), polynuclear aromatic hydrocarbons (PNAs), and carbon monoxide (CO). All job categories on two of the six pot lines were monitored for two successive shifts. Excessive exposures to fluorides were measured among the crane operators, particularly among cranemen involved with placement of new carbon anodes in the pots. The four personal samples obtained from cranemen ranged from 0.95 to 3.61 milligrams fluoride per cubic meter of air (mg/m^3), averaging 2.31. The NIOSH Recommended Exposure Limit for fluorides is $2.5 \text{ mg}/\text{m}^3$. No other overexposures were measured for any of the previously mentioned compounds among the other job categories.

From June 25 to July 18, 1985, NIOSH investigators conducted a cross-sectional medical questionnaire survey. All potroom employees and a sample of employees from other departments were invited to participate. Six hundred fifty employees completed the questionnaire (74% of the 879 eligible). One hundred (16%) reported symptoms suggestive of asthma, but only 32 reported a history of asthma. Of the 24 who reported asthma confirmed by a doctor, 17 still had it. In 13 of these cases, 2.5% of the 521 participants who had ever worked in the potroom, the asthma was temporally related to work, and symptoms were worse in or near the potroom. Six of the 13 cases were in current potroom workers, each from a different pot line. Pot room-related, physician-confirmed asthma was not associated with age, smoking status, years at Ormet, or years in the potroom.

Four neurologic effects -- memory impairment, cognitive dysfunction, anxiety, and neurasthenic symptoms -- were no more prevalent among current potroom workers than among other participants, but each was more prevalent among workers who had ever worked in the potroom. For none of the four neurologic effects, however, did the group reporting it have a higher mean number of years worked in the potroom than the group not reporting it.

Environmental monitoring identified a potential for excessive exposures to fluorides among crane operators in the potrooms. Although a number of workers reported a history of asthma temporally related to work in or near the potroom, the epidemiologic analysis did not identify any risk factors that would support the hypothesized etiologic role of exposures in the potroom. To the extent that time in the potroom is an indicator of aluminum exposure, this study did not provide convincing evidence of an association between neurologic effects and aluminum exposure. Recommendations for reducing exposure to fluorides are presented in Section VIII of this report.

KEYWORDS: SIC 3334 (Primary Production of Aluminum), Aluminum, Fluorides, Sulfur Dioxide (SO₂), Polynuclear Aromatic Hydrocarbons (PNAs), Coal Tar Pitch Volatiles (CTPVs), Carbon Monoxide (CO), Pot Room, Asthma, Neurologic

II. INTRODUCTION

On July 6, 1984, NIOSH received a request for health hazard evaluation from the Chairman of the Safety and Health Committee of Local 5724, United Steelworkers of America, to evaluate complaints of respiratory and skin irritation among employees of the Ormet Corporation, Hannibal, Ohio. This facility produces primary aluminum. In addition, carbon anodes are manufactured for use in the aluminum reduction operations.

An initial visit was conducted in August 1984, where NIOSH investigators met with management and employee representatives to further define the nature of the request, with the goal of developing an evaluation protocol. At that time, union officials expressed employee concerns about possible health effects from long-term exposure to potroom gases, fumes, and dusts. Many workers believed that exposures had grown worse from changes in the ventilation systems in the potrooms. Also, several workers were worried about the significance of high urinary fluoride levels among potroom workers. In 1983, the last complete calendar year preceding the initial visit, seven (14%) of 50 urine fluoride concentrations in crane operators, and 5 (10%) of 51 from carbon setters, exceeded 7 micrograms per liter (ug/l), the level in post-shift urine indicative of excessive exposure to fluoride (the level in pre-shift urine indicative of excessive exposure is 4 ug/l).¹ In other job categories, 2-3% of urine fluoride concentrations exceeded 7 ug/l.

From information collected during the initial site visit, the NIOSH investigators determined the need for an industrial hygiene and epidemiologic survey to determine whether employees were being exposed to hazardous levels of potroom gases and fumes, and if health effects (particularly respiratory and neurologic symptoms) were associated with work in the potrooms. A medical questionnaire was distributed to employees in June and July, 1985. Results of the respiratory portion of the medical survey were reported to the company and union on April 15, 1988. In April 1988, an industrial hygiene evaluation was conducted, evaluating exposures among a cross-section of potroom employees.

III. BACKGROUND

The Hannibal Ormet facility was constructed and began production of primary aluminum in 1957. The plant also contains a facility for production of carbon anodes, which are used in the aluminum reduction process.

The facility has six potrooms, with each potroom consisting of two buildings each. These buildings are 1000 feet long, housing 86 pots, for a total of 1032 pots. The "pots" are rectangular steel tanks with linings of refractory bricks to resist heat and the corrosive effects

of the fluorides. In the pots, aluminum oxide (alumina) is reduced to nearly pure metallic aluminum in a bath of molten fluorides, at a temperature of approximately 1800°F. Because of the high melting point of aluminum oxide, the alumina cannot be smelted by thermal reduction with coke (as is iron ore); rather, reduction energy must be supplied electrolytically. Carbon electrodes are used as the anode, and the aluminum metal in the pot acts as the cathode. The passage of current causes the heavier metal to sink to the bottom of the pot. Oxygen combines with the carbon from the anodes and is liberated as carbon dioxide and carbon monoxide. The bath above the molten aluminum contains the alumina and fluoride electrolytes at temperatures at approximately 1800 °F. An insulating frozen crust of this bath material remains on the surface. Cryolite is the main fluoride compound used in the process. This material dissolves up to 20% of its weight in alumina and reduces the melting point of the ore. Fluorspar is also added to lower the melting point of the mixture, and aluminum fluoride is present to increase current efficiency.

As previously mentioned, pre-baked carbon blocks, approximately 300 pounds each, with a copper rod inserted through their middle, act as the anodes. These blocks are systematically replaced (approximately every 14 days) as the carbon material is gradually consumed in the process. Molten aluminum is removed ("tapped") from each pot every 32 hours, at a tap rate of approximately one ton per pot.

Each pot is enclosed with removable panels and provided with local exhaust ventilation to remove the fumes and gasses at an average rate of 2500 cubic feet per minute per pot. The pot effluents are passed through air pollution control equipment prior to release to the atmosphere. Other engineering controls are present on the dump chutes and ore bins.

Following are descriptions of the jobs monitored during the environmental evaluation. The number of employees per job on a typical line are in parentheses.

Potman - (6) Their primary responsibility is to monitor the operation of the pots. Periodically, they must break the insulating crust on the pot, add aluminum ore, and align the anodes. Also, short circuits or arcs must be stopped using wooden probes inserted to the bottom of the pots to break up air gaps in the molten material. Each of the six potmen tends 29 pots/shift.

Tapper - (2) These employees remove the molten aluminum from the bottom of the pots by placing a vacuum tap through an end access port, forcing the molten metal into a large evacuated crucible. Each tapper is responsible for 1/4 of a potline/shift. One pot requires 1/2 to one hour to tap. The tappers are also responsible for cleaning the crucible.

Setter - (3) Spent carbon anodes are removed and the excess carbon knocked off via sledge hammer, and the copper rod inserts are returned to the carbon plant. Fresh anodes are then placed into the pots with the assistance of an overhead crane. Each setter is responsible for 1/4 of a pot line per shift.

Utility - (2) The utility, or PRU, job entails assisting the other operators, adding ore and other constituents to the pots, and other miscellaneous tasks.

Craneman - (2) The cranemen operate the overhead cranes and move spent rods from the pots, position new carbon anodes, transport and add alumina via portable bins, and move all equipment for the tapping operation. The cranemen are classified as either "tapper" (removal of molten aluminum) or "setter" (placement of new carbon anodes).

Metal Truck - (1) Molten aluminum is transported to a neighboring cast facility in large crucibles on carts.

Line "2" has been computerized, reducing the manual labor requirements for several of the jobs, including breakage of the surface crust for addition of ore.

IV. EVALUATION DESIGN AND METHODS

A. Environmental

Environmental samples were collected in the breathing zone (personal samples) of potroom employees by attaching the appropriate sampling media in line with pre-calibrated environmental sampling pumps, which were attached to their belt. These samples were collected for the duration of the shift. Two sequential day and evening shifts were monitored; two shifts from a computerized potroom, and two from a potroom typifying all other potrooms. It was deemed important to monitor the computerized "line" since there were plans to convert a portion of the existing lines to computer-operated lines. Measured contaminants included fluorides, sulfur dioxide (SO₂), coal-tar pitch volatiles (CTPV), polynuclear aromatic hydrocarbons (PNAs), and carbon monoxide. Following is a description of the sampling and analytical methods used for each compound.

Fluorides: Twenty-five personal samples for fluorides were collected using 37-millimeter (mm) cassettes containing mixed cellulose ester (MCE) filters and a cellulose O-ring to collect particulate fluoride, followed by a second 37-mm cassette containing a treated backup pad to collect gaseous fluoride

compounds (NIOSH Method #7902).² Sample flow rates were pre-calibrated at 2 liters per minute (lpm) and monitored periodically during the work shift. For analysis, each MCE filter sample was transferred to a crucible. The sample was then fused with 5 milliliter (ml) of 20% sodium hydroxide to dissolve the particulate fluoride compounds. All samples contained particulate on the inside wall of the cassette. The samples were transferred carefully and the particulate clinging to the inside of the cassette was transferred with a camel's hair brush. Because these samples were so heavily loaded with particulate, transfer of the particulate was not quantitative. After the NaOH fusion, the samples were dissolved in deionized water and diluted by a factor of 40 prior to analysis using ion chromatography (IC). Each treated backup pad was transferred to a plastic scintillation vial. Twenty ml of deionized water was added and the samples were placed in a sonic bath for 5-10 minutes. The samples were diluted by a factor of 10 prior to analysis. However, it was necessary to dilute some samples by a factor of 100 for analysis. All samples were analyzed by IC under the following instrumental conditions:

IC:	Dionex 2010i
Columns:	AG4A Guard, AS4A Analytical
Suppressor:	Anion Micromembrane
Eluent:	5 mM $\text{Na}_2\text{B}_4\text{O}_7$
Flow Rate:	2.0 mL/min.
Detector:	Conductivity, 10 uS scale
Injection Vol:	50 uL
Retention Time:	1.8 minutes

Additional studies to determine the effect of aluminum on the analysis of fluoride by IC were performed in conjunction with the analyses of these samples. Weighed portions of cryolite (Na_3AlF_6) were taken through the fusion procedure used in the particulate fluoride analysis. The fused cryolite samples were analyzed by IC under the same conditions as the field samples, and the recoveries for fluoride were 98-100%. In addition, fluoride standards were spiked with aluminum to investigate the effect of aluminum on the quantitation of fluoride by IC. Low levels of aluminum (less than 1 ug/ml) had no effect on the quantitation of fluoride. Higher concentrations of aluminum reduced the height of the fluoride peak, but had little effect on the peak area. Five environmental air samples were collected from the potrooms and analyzed for aluminum as part of this study. The airborne aluminum concentrations found from these samples ranged from 0.35 - 1.3 mg Al/m^3 . The largest air volume sampled for fluoride was 0.924 m^3 . If this sample contained the highest concentration of Al found in this study, the effective dilution volume for the fused samples of 1600 ml would give an aluminum concentration of less

than 1 ug/ml. Therefore, aluminum was not expected to cause interference problems in the IC quantitation of fluoride. That was, in fact, the case for the field samples, as there was no difference in the results regardless of whether peak height data or peak area data were used for calculations.

The limit of detection (LOD) for the treated backup pad samples was 1 ug (microgram) F⁻/sample. The limit of quantitation was 3.3 ug F⁻/sample. The LOD for the MCE filters taken through the fusion procedure was 16 ug F⁻/sample, and the LOQ was 64 ug F⁻/sample.

Sulfur Dioxide: Nine personal samples were collected for SO₂ using 37-mm MCE filters followed by potassium hydroxide-treated 37-mm cellulose filters at a pre-calibrated flow rate of 1.5 lpm, according to NIOSH method 6004.² The samples were analyzed for sulfate ion concentrations by ion chromatography. The filter of each sample was separately desorbed in 10 ml of eluent and allowed to stand with occasional shaking for 30 minutes. One drop of 30% hydrogen peroxide was then added to each sample. The resulting solutions were filtered through a 0.45 micron filter, and an aliquot was analyzed by a Dionex 2010 ion chromatograph equipped with a WISP 710B autosampler. Liquid standards covering the range 0.25 to 15.0 micrograms sulfate ion per milliliter were prepared and analyzed with the samples. The following instrumental conditions were used:

Eluent:	0.68 nm NaHCO ₃ /2.0 nm Na ₂ CO ₃
Flow Rate:	2.0 ml/minute
Detection Setting:	30 ug (Full Scale)
Columns:	HPIC-AG4A Pre-column HPIC-AS4A Separator AMMS-1 Membrane Suppressor

The NIOSH limit of detection was calculated to be 4 ug sulfate ion/sample. The limit of quantitation was calculated to be 12 ug sulfate ion/sample.

Coal Tar Pitch Volatiles - Polynuclear Aromatic Hydrocarbons: Seventeen personal samples were collected for CTPVs and PNAs according to NIOSH methods 5023 and 5515, respectively.³ A 2-um pore size, 37-mm PTFE membrane filter followed by a washed XAD-2 tube (ORBO-43, 150-mg) was used at a flow rate of 2.0 lpm. Filters were contained in opaque cassettes and tubes were wrapped in aluminum foil and shipped on ice, to prevent sample degradation from heat and UV prior to analysis. For CTPV analysis, the PTFE filters were placed in screw-cap vials with 5-ml of benzene and sonicated for 30 minutes. The extract was filtered through a 0.45-um nylon filter and collected in an additional test tube. One

ml of the sample was then transferred into a tared Teflon cup and evaporated to dryness in a vacuum oven at 40° C. The Teflon cup was again weighed and the difference recorded, the weight gain of the cup being one-fifth the total benzene solubles per sample. The limit of detection for benzene solubles was 0.05 mg per sample.

For PNAs, the ORBO-43 tubes and PTFE filters were analyzed by gas chromatography according to NIOSH Method 5515 with the following modifications:

Extraction: 5.0-ml of benzene with 30 minutes sonication.
 Gas Chromatograph: Hewlett-Packard Model 5711A equipped with a flame ionization detector.
 Column: 30-m x 0.32-mm fused silica capillary column coated internally with 1.0 micron DB-5.
 Oven Conditions: Temperature programmed from 115 °C to 290 °C at a rate of 4 °C per minute.

Following are the NIOSH calculated LODs and LOQs for the tube and filter samples, in nanograms/sample:

	ORBO-43		PTFE	
	LOD	LOQ	LOD	LOQ
Naphthalene	0.5	1.8	0.5	---
Acenaphthylene	0.3	---	0.3	---
Acenaphthene	0.3	---	0.3	---
Fluorene	0.3	---	0.5	---
Phenanthrene	0.3	1.0	0.5	---
Anthracene	0.3	---	0.5	---
Fluoranthene	0.3	---	0.5	1.7
Pyrene	0.3	---	0.5	---
Benz(a)anthracene	0.3	---	0.5	---
Chrysene	0.3	1.0	1.0	---
Benzo(b)fluoranthene	0.3	---	1.0	---
Benzo(k)fluoranthene	0.3	---	0.5	1.6
Benzo(e)pyrene	0.3	---	0.5	---
Benzo(a)pyrene	0.3	---	1.0	---
Indeno(1,2,3-cd)pyrene	1.0	---	1.0	---
Dibenz(a,h)anthracene	1.0	---	1.1	3.7
Benzo(ghi)perylene	0.5	---	1.0	---

Carbon Monoxide: Nine personal samples for carbon monoxide were obtained using commercial long-term length of stain tubes. These samples were collected for the duration of the work shift at 20 cubic centimeters of air/minute.

Several samples for airborne ammonia were obtained at various locations using Dräger length of stain indicator tubes. These tubes are useful for determining indications of airborne contamination. The accuracy of the tubes ranges from ± 25 to 35%.

B. Medical

From June 25 to July 18, 1985, NIOSH investigators conducted a cross-sectional medical questionnaire survey. All potroom employees and a sample of employees from other departments were invited to participate. The questionnaire focused on respiratory and neurologic symptoms. The neurologic symptom questions included those adapted from the "Swedish 16" screening questionnaire.⁴ Although work history records were obtained from the company, determination of participant work histories from these records proved quite cumbersome, so the self-reported work history information from the questionnaires was used instead.

V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists^o (ACGIH) Threshold Limit Values (TLVs), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations

and ACGIH TLVs are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLVs usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure generally refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. For the purposes of this evaluation, exposures were time-weighted for the duration of the sampling period (i.e., non-sampled periods were not treated as "zero" exposure). Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

Fluorides: The primary concerns for occupational fluoride exposure are irritation of the mucous membranes and the skin, and chronic effects on the bones ranging from mottling of tooth enamel to skeletal abnormalities. The NIOSH REL of 2.5 mg/m^3 was designed to "...prevent the occurrence of deleterious health effects resulting from fluoride deposition."¹ This exposure limit is supported by the ACGIH, ANSI, and others.

Respiratory irritation may result from inhalation of fluorides in the form of dusts. Chronic fluoride intoxication can result from long-term, even low grade exposures to fluorides in whatever chemical combination, and either particulate or gaseous.

Historically, in what was described as "heavily exposed" cryolite workers, effects included nausea, vomiting, loss of appetite, diarrhea, or constipation in more than 80% of a population exposed at an estimated concentration of 15 to 20 mg/m^3 . Characteristic increased bone density was found among slightly more of the workers than those showing digestive disturbances, presumably resulting from levels greater than 20 mg/m^3 . Significantly more digestive tract disturbances were found in a group of aluminum furnace room workers in Great Britain exposed at levels of 0.14 to 3.43 mg/m^3 , as compared to a control group. Nearly all of a group of aluminum potroom workers in the U.S. had increased bone density following TWA exposures of 2.4 to 6.0 mg/m^3 . All of these reported studies, however, lacked data on historic exposure, which was suspected to be higher than measured at the time of the evaluation. The basis for the ACGIH TLV for fluorides, and the criteria updated in 1976 by the NIOSH REL, involves a study of fertilizer manufacturing workers which detailed exposures of between 1.78 and 7.73 mg/m^3 (and supported by biological monitoring). Of the 74 employees, only minimal or questionable skeletal fluorosis was found in 23%. Of these 23%, 71% were exposed to TWA concentrations of greater than 2.5 mg/m^3 .

Sulfur Dioxide: Sulfur dioxide is irritating to the upper respiratory tract. Chronic exposure can cause runny nose, dryness of the throat, and cough. Long-term low-level exposure can cause chronic bronchitis and reduced pulmonary function. In 1977, in testimony before the Department of Labor, NIOSH revised its REL for SO₂ from 5.2 mg/m³ to 1.3 mg/m³.⁵ This revision was based on epidemiologic and exposure data indicating acute and chronic health effects observed in the 2.6 to 13 mg/m³ exposure range. Consideration was also given to: 1) health effects observed among workers and experimental subjects in the 2.6 - 5.3 mg/m³ range, 2) the ten to 20 percent of the population who are especially susceptible to SO₂ effects, 3) the possibility that synergistic effects with other aerosols or gases may occur, 4) the possibility of an increased fraction of SO₂ reaching the lower lungs through mouth breathing or because of rapid or deep breathing, 5) the possibility that SO₂ may act as a cancer promoting agent, 6) the possible enhancement of effects by high humidity, and 7) the likelihood that degradation products (sulfites and sulfates) will accompany SO₂ exposure.

Coal Tar Pitch Volatiles - Polynuclear Aromatic Hydrocarbons: Several PNAs, such as benzo(a)anthracene and pyrene, have been shown to be carcinogenic in animals. Excess risk of lung cancer, oral cancer, and skin neoplasms (benign and malignant) have been found in working populations handling coal-tar products which NIOSH has defined to include coal-tar, coal-tar pitch, and creosote.⁶ A TWA exposure of 0.2 micrograms (ug)/m³ was recommended by the coke oven advisory committee for benzo(a)pyrene under the OSHA 29 CFR 1910.1029 coke oven emissions standards, but was not adopted, and a special NIOSH hazard review of chrysene recommended that it be controlled as an occupational carcinogen. Also, ACGIH includes chrysene and benzo(a)pyrene in its list of industrial substances suspected of human carcinogenic potential.⁷ The carcinogenic potential of other PNAs (benzo(a)anthracene, anthracene, pyrene, and fluoranthene) has also been documented.⁶

The acute toxic effects of exposure to coal-tar pitch include skin and mucous membrane irritation mediated directly and, more noticeably, through phototoxic reactions involving an interaction between PNAs and ultraviolet (UV) radiation. Most phototoxic relations require UV-A radiation in the range of 320-400nm. The mechanism involves the absorption of this radiant energy by the skin and by the PNAs on the skin which can then result in cell changes.⁸ As expected, these reactions affect outdoor workers who handle these materials and receive exposure to sunlight.

Thus these reactions are more frequent and severe in the summer and during mid-day when UV radiation is most intense. The effects most often described include erythema (reddening of the skin) and

conjunctivitis (inflammation of the lining of the eyelid and white part of the eye). The onset of symptoms are reported to be delayed until the day after exposure when the pitch worker goes outdoors and receives UV light that can interact with the PNAs on the skin. Elimination of either the light or contact with the phototoxic substance eliminates the problem. Increased skin pigmentation (melanin) has been shown to have a protective effect.

Historically, occupational exposures to PNAs were estimated by determining exposures to the "soluble" fraction of the airborne particulate. Research indicated that if the soluble portion (benzene was usually used as the solvent for extraction) of the particulate was less than a specified level (0.2 mg/m^3 OSHA PEL; 0.1 mg/m^3 NIOSH REL) exposures to the airborne PNAs should be below levels expected to result in adverse health effects (based upon laboratory animal experiments). This "surrogate" methodology was employed due to the difficulty in analyzing for specific PNAs. Recently, advances in analytical chemistry have enabled the direct measurement of the potentially carcinogenic PNAs. However, for comparison purposes, and because the NIOSH REL and OSHA PEL have not been updated to reflect these improved analytical capabilities, both evaluative techniques were employed during the survey (i.e., measurement of both CTPVs and individual PNAs).

Carbon Monoxide: Carbon monoxide (CO) is a colorless, odorless, tasteless gas produced by incomplete burning of carbon-containing materials. Major sources of human exposure to CO are engine exhaust, tobacco smoking, and inadequately ventilated combustion products from appliances and heaters that use natural gas, propane, kerosene, or similar fuels. On inhalation, CO acts as a metabolic asphyxiant, causing a decrease in the amount of oxygen delivered to the body tissues. CO combines with hemoglobin (the oxygen carrier in the blood) to form carboxyhemoglobin, which reduces the oxygen-carrying capacity of the blood. The initial symptoms of CO poisoning may include headache, dizziness, drowsiness, and nausea. These initial symptoms may advance to vomiting, loss of consciousness, and collapse, if prolonged or high exposures are encountered. Coma and death may follow if high exposures continue without intervention. Long-term, low-level exposure to CO can increase the risk of heart attack for some people.^{9,10}

The criteria used to evaluate occupational exposure to CO are:

OSHA	50 ppm* TWA
NIOSH	35 ppm TWA 200 ppm Ceiling
ACGIH	50 ppm TWA 400 ppm Short Term Exposure Limit

* ppm = CO per million parts of air

VI. RESULTS AND DISCUSSION

A. Environmental

1. Fluorides

Tables 1-4 present composite results of environmental sampling for all compounds by shift and operation. The following is a summary of TWA exposures to fluorides by job category.

<u>Job</u>	<u>No. of Samples</u>	<u>Range (mg/m³)</u>	<u>Average (mg/m³)</u>
Potmen	9	0.02 - 0.96	0.47
Setters	3	1.45 - 2.14	1.70
Tappers	2	0.40 - 0.49	0.45
Utility	3	0.25 - 1.14	0.64
Crane	4	0.95 - 3.61	2.31
Truck	2	0.14 - 0.43	0.29

As indicated, exposure to airborne fluorides was fairly consistent across the job categories. Most notable among measured exposures were those to the crane operators, where two of the four samples exceeded the evaluation criteria of 2.5 mg/m³. These excessive exposures were measured while the crane operators were assisting in "setting" carbon. The two lower exposures were monitored from crane operators assisting in tapping molten aluminum (movement of crucible and related equipment). Employees engaged in actually setting carbon had the next highest level of exposure, suggesting that this operation may present the highest potential for exposure to fluorides in the potroom. These results are consistent with the 1983 urinary fluoride data (previously discussed). Of the samples for fluorides other than those obtained from employees

engaged in setting carbon (cranemen and carbon setters), the gaseous fraction of the total fluoride exposure averaged 20%. For carbon setting jobs (including setter cranemen) the gaseous fraction ranged from 19 to 70%, averaging 49%, indicating a substantial difference in the form of fluoride exposure between job categories (i.e., gaseous vs. particulate). The form of the airborne exposure will impact the appropriate type of respiratory protection, due to the potential for acid-gas formation in the presence of gaseous fluorides.

2. Sulfur Dioxide

Following is a summary of exposures to SO₂ by job category.

<u>Job</u>	<u>No. of Samples</u>	<u>Range (mg/m³)</u>	<u>Average (mg/m³)</u>
Potmen	4	0.15 - 0.50	0.35
Setters	2	ND - 0.68	NA
Tappers	4	0.16 - 0.30	0.21
Crane	1	0.37	NA

(LOD = 4 ug/sample; LOQ = 12 ug/sample)

As indicated, TWA exposures to SO₂ were below the criteria of 1.3 mg/m³ for all jobs monitored.

3. Polynuclear Aromatic Hydrocarbons/Coal Tar Pitch Volatiles

None of the 17 PNAs monitored were present in measurable quantities. Considering the analytical limits of detection (0.3 - 1.0 ug/sample) and the average air volume sampled (approximately 0.8 m³), the lowest measurable concentration corresponds to airborne concentrations of less than 0.4 - 1.3 ug/m³.

The following presents airborne concentrations of CTPVs measured during the environmental survey.

<u>Job</u>	<u>No. of Samples</u>	<u>Range (mg/m³)</u>	<u>Average (mg/m³)</u>
Potmen	6	ND - 0.32	0.14
Setters	4	ND - 0.20	0.05
Tappers	2	ND - ND	NA
Utility	3	0.09 - 0.30	0.18
Truck	1	ND	NA

As discussed earlier, historic evaluation of exposure to the carcinogenic PNAs was limited to measurement of the soluble fraction of the particulate exposure. However, current analytical capabilities enable actual measurement of the 17 "priority" PNAs (as defined by the Environmental Protection Agency)³, rather than use of a "surrogate". As indicated by the environmental data, even though the OSHA PEL and the NIOSH REL are exceeded for CTPV, there were no measurable exposures to the PNAs evaluated.

4. Carbon Monoxide: Exposures to CO ranged from 3 to 9 mg/m³; the nine sample results averaged 5 mg/m³. No overexposure situations were indicated from this environmental data.

5. Ammonia: During a "wash down" (routine maintenance of inoperative pot) on line #5, several detector tube samples for airborne ammonia were collected in the general area. Airborne concentrations ranged from 30 ppm on the floor level near the pot, to 100 ppm on the "bridge" between the pots. The NIOSH REL for ammonia is 50 ppm as a 5-min. ceiling concentration. While this may indicate a problem area, the detector tubes used for determining airborne concentrations of ammonia at the pot line have accuracies of only $\pm 25 - 50\%$.

B. Medical

Six hundred fifty employees completed the questionnaire, 74% of the 879 eligible. Departmental participation rates ranged from 45% in the furnace room to 95% in the rodding room. In the potroom, which had the most employees (434), the participation rate was 73%. Participants ranged in age from 23 to 72 years, with a mean and median of 41. Of the 628 who specified their sex, 593 (94.4%) were male, and 35 (5.6%) were female. Of the 644 for whom cigarette smoking status could be determined, 246 (38.4%) never smoked, 203 (31.9%) were current smokers, and 191 (29.8%) were former smokers.

The participants worked from 1 to 28 years at Ormet, with a mean of 14 and median of 15. Three hundred sixteen (49%) were in the potroom department, 6 (1%) in pot service, and 328 (50.5%) in other departments. Comparable numbers of participants from each of the pot lines participated.

Of the 548 who provided adequate information to determine level of chronic shortness of breath (SOB), 127 (23%) had mild SOB, 99 others (18%) had moderate SOB, and 58 others (11%) had severe SOB. Of the 625 who answered the question, 286 (46%) reported having had wheezing; 100 (16% of the 625) reported symptoms suggestive of asthma (attacks of wheezing with normal breathing between attacks). However, to the question asking directly about a history of asthma, only 32 (5% of all participants) reported ever having it, and only 24 said that it was confirmed by a doctor. Of these 24, 17 said that they still had asthma. In 4 of the 17 cases, the asthma was non-occupational; that is, it was the same or worse away from work. In the remaining 13 cases (2% of the 650 participants, 2.5% of the 521 who ever worked in the potroom), all said that their symptoms were better away from work and worse when working in or near the potroom. Six of the 13 cases were in

current potroom workers; each worked on a different pot line. (Among the 8 reported asthma cases not confirmed by a doctor, one had worse symptoms in or near the potroom, and another had symptoms worse at work but not associated with the potroom.) Potroom-related, physician-confirmed asthma, as described above, was not associated with age, smoking status, years at Ormet, or years in the potroom (Table 5).

For the purpose of analyzing the neurologic symptom questions, we grouped neurologic effect questions as shown in Table 6. We considered an effect to be present if any one of its symptoms was reported. Current potroom workers did not have a higher prevalence of any of the four neurologic effects than other workers (Table 7). Workers who had ever worked in the potroom had a higher prevalence of each effect than those who had never worked in the potroom, even though the potroom workers were younger (mean age = 39.2 years, standard deviation = 10.2, number of participants = 502; versus 46.6, 9.7, 94; $t = 6.45$, $p = 0.0001$). For none of the four neurologic effects, however, did the group reporting it have a higher mean number of years worked in the potroom than did the group not reporting it (Table 8), and for each effect the two groups were of comparable age. Because the prevalences of neurologic effects, as defined above, were relatively high, we re-analyzed the data using a more restrictive definition - the presence of at least two symptoms (Table 6). Except for lower prevalences, this analysis yielded similar findings.

VII. CONCLUSIONS

Environmental monitoring identified a potential for overexposures to fluorides among crane operators, with the gaseous fraction of the exposure exceeding the particulate fraction. The next highest exposure group among potroom employees was the setting crew. Again, their fluoride exposures were shown to consist primarily of the gaseous fraction. Occupational exposure to fluorides, as defined in the NIOSH criteria document, includes exposures to one-half the NIOSH REL (i.e., 1.25 mg/m^3). In this context, exposures are limited to the Setting and Crane job categories. The significance of the gaseous fraction of the airborne exposure involves the requirements for respiratory protection; i.e., with exposure to fluoride gas, acid-gas cartridges are required.

Although a number of workers reported a history of asthma temporally related to work in or near the potroom, the epidemiologic analysis did not identify any risk factors that would support the hypothesized etiologic role of exposures in the potroom. The presence of selected neurologic effects was not associated with current employment in the potroom. Although neurologic effects appeared to be more prevalent among participants who had ever worked in the potroom, the presence of the effects was not associated with time in the potroom. Thus, to the extent that time in the potroom is an indicator of aluminum exposure, this study did not provide convincing evidence of an association between neurologic effects and aluminum exposure.

VIII. RECOMMENDATIONS

Based upon the environmental monitoring and the observations made during this evaluation, the following recommendations are made to reduce the potroom employees' occupational exposures.

1. Engineering controls should be implemented to reduce the crane operators' exposure to fluorides.
 - a. Engineering controls may take the form of source controls (i.e., control of the emissions from the pots) or control of the exposure at the worker's position (i.e., enclosure of the crane cab). Enclosure of the crane cabs would seem most feasible. This will involve the installation of positive pressure, air filtration devices and assurances that safety is not compromised by obscuring/obstructing the operator's hearing or vision. NIOSH's Division of Physical Science and Engineering (DPSE) is available for supplying details and/or analysis of methods to enclose the crane cabs. At least one demonstration project has been conducted under contract to DPSE involving enclosure of an operator's cab in an environment contaminated with acid gasses.
 - b. In the interim, the current respiratory protection program should include acid-gas cartridges for Crane Operators and Setters. All respirator use should be accompanied by a complete respirator program as described in the OSHA standards, 29 CFR 1910.134.
2. Exhausting the crucible to the plant atmosphere (during tapping of molten aluminum from the pots) is creating an unnecessary exposure situation. If feasible, the crucible should be exhausted to the outside.

3. Eating and drinking in the break room (near the supervisor's office at each pot line) should not be allowed. Ingestion is a very efficient method for absorption of fluorides. Because there are no effective methods for cleaning these areas, or easily accessible areas for the employees to wash their hands prior to eating at these locations, the potential for increasing their occupational exposure to fluorides through ingestion should be considered.
4. Strict maintenance of the pot access doors and shields is necessary to provide adequate exhaust ventilation. Many of the access doors were observed either ajar or loosely fitted.
5. Follow-up environmental monitoring for airborne ammonia should be conducted during the "wash down" of pots. Detector tube samples collected during this operation indicated a potential overexposure situation.
6. Workers required to use respirators should have appropriate medical evaluations,¹¹ and workers exposed to fluoride should have periodic monitoring of urine fluoride concentrations.¹ Elevated urine fluoride concentrations in an individual or in a group, should trigger evaluation of the work environment and implementation of appropriate controls.¹

IX. REFERENCES

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XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are temporarily available upon request from NIOSH, Hazard Evaluations and Technical Assistance Branch, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. Ormet Corporation, Hannibal, Ohio
2. United Steelworkers of America, Local 5724
3. NIOSH, Region V
4. OSHA, Region V

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE 1
ENVIRONMENTAL AIR SAMPLING RESULTS
1st Shift, Line 2
April 6, 1988

HETA 84-426
Ormet Corporation
Hannibal, Ohio

No.	Operation	Duration	Exposure Concentration (mg/m ³)			
			Fluorides	SO ₂	CO	Benzene Solubles
F-1	Potman	0745 - 1427	0.19			
F-6	Potman	0804 - 1430	0.51			
F-4	Cross Over Potman	0755 - 1322	0.68			
S-3	Potman	0819 - 1451		0.50		
P-2	Potman	0810 - 1454				0.31
F-3	Setter	0753 - 1422	1.45			
S-2	Setter	0800 - 1426		0.68		
P-1	Setter	0807 - 1424				0.20
F-2	Tapper	0748 - 1416	0.40			
S-1	Tapper	0750 - 1416		0.16		
F-5	Crane	0802 - 1440	1.41			
C-2	Crane	0759 - 1424			7	
P-3	Utility	0814 - 1434				0.15
P-4	Utility	0915 - 1432				0.30
C-3	Utility	0813 - 1446			5	
F-7	Truck Driver	0827 - 1449	0.43			

EVALUATION CRITERIA:

2.5 1.3 39 0.10*

* See text for discussion of applicability; no measurable quantities of PNAs

TABLE 2
ENVIRONMENTAL AIR SAMPLING RESULTS
2nd Shift, Line 2
April 6, 1988

HETA 84-426
Ormet Corporation
Hannibal, Ohio

No.	Operation	Duration	Exposure Concentration (mg/m ³)		
			Fluorides	SO ₂	CO Benzene Solubles
F-10	Potman	1530 - 2221	0.02		
F-11	Potman	1532 - 2214	0.58		
S-12	Potman	1555 - 2231		0.29	
P-10	Potman	1613 - 2216			0.21
P-11	Cross Over Potman	1552 - 2147			ND*
C-21	Potman	1608 - 2246			3
C-20	Setter	1619 - 2210			8
P-11	Setter	1617 - 2211			ND
S-11	Tapper	1543 - 2158		0.20	
P-14	Tapper	1550 - 2215			ND
F-13	Utility	1549 - 2155	0.53		
F-12	Utility; Sweep	1638 - 2217	1.14		
P-12	Truck Driver	1615 - 2314			ND
F-14	Crane	1537 - 2218	3.61		
S-10	Crane	1535 - 0926		0.37	
EVALUATION CRITERIA:			2.5	1.3	39 0.10**

* ND = None Detected (LOD = 0.05 mg/sample)

** See text for discussion of applicability; no measurable quantities of PNAs

TABLE 3
ENVIRONMENTAL AIR SAMPLING RESULTS
1st Shift, Line 6
April 7, 1988

HETA 84-426
Ormet Corporation
Hannibal, Ohio

No.	Operation	Duration	Exposure Concentration (mg/m ³)			
			Fluorides	SO ₂	CO	Benzene Solubles
F-20	Potman	0742 - 1428	0.34			
F-21	Potman	0745 - 1443	0.96			
F-22	Cross Over Potman	0748 - 1425	NA*			
S-22	Potman	0816 - 1445		0.15		
P-22	Potman	0804 - 1434				0.32
C-30	Potman	0750 - 1433			5	
F-23	Setter	0749 - 1430	1.51			
S-20	Setter	0753 - 1424		ND**		
P-23	Setter	1016 - 1429				ND
F-24	Tapper	0751 - 1435	0.40			
S-21	Tapper	0758 - 1436		0.19		
F-26	Crane	0823 - 1439	0.95			
C-22	Crane	0758 - 1430			9	
F-25	Metal Truck	0814 - 1437	0.14			
P-21	Utility	0802 - 1426				0.09
C-23	Utility	0800 - 1430			6	
EVALUATION CRITERIA:			2.5	1.3	39	0.10***

* NA = Not Analyzed (tube broken in transit to laboratory)

** ND = None Detected (LOD = 0.05 mg/sample)

*** See text for discussion of applicability; no measurable quantities of PNAs

TABLE 4
ENVIRONMENTAL AIR SAMPLING RESULTS
2nd Shift, Line 6
April 7, 1988

HETA 84-426
Ormet Corporation
Hannibal, Ohio

No.	Operation	Duration	Exposure Concentration (mg/m ³)			
			Fluorides	SO ₂	CO	Benzene Solubles
F-33	Potman	1519 - 2218	0.29			
F-30	Potman	1545 - 2216	0.64			
P-30	Potman	1517 - 2211				ND*
P-31	Cross Over Potman	1520 - 2138				ND
C-30	Potman	1523 - 2210			2	
S-31	Potman	1559 - 2222		0.47		
F-35	Setter	1641 - 2139	2.14			
P-33	Setter	1536 - 2137				ND
C-31	Setter	1524 - 2135			4	
P-32	Tapper	1530 - 1715				ND
S-32	Tapper	1526 - 2149		0.30		
F-31	Crane	1529 - 2116	3.25			
F-34	Utility	1521 - 2203	0.25			

EVALUATION CRITERIA:	2.5	1.3	39	0.10**
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* ND = None Detected (LOD = 0.05 mg/sample)

** See text for discussion of applicability; no measurable quantities of PNAs

TABLE 5

POTENTIAL RISK FACTORS FOR POTROOM-RELATED ASTHMA¹

Ormet Aluminum
Hannibal, Ohio
HETA 84-426
June 25-July 18, 1985

<u>Potential risk factor</u>	<u>Potroom-related asthma</u>		<u>Statistical comparison²</u>
	<u>Present</u>	<u>Absent</u>	
Age (years)	12; 41 \pm 8.9*	579; 40 \pm 11.8	t = 0.33 p = 0.80
Ever smoked			
Yes	9	360	RR = 1.9
No	3	227	95% C.I.: 0.5-6.7
Years at company	13; 13.9 \pm 9.0	594; 14.3 \pm 9.3	t = 0.14 p = 0.89
Years in potroom	13; 9.6 \pm 6.9	571; 7.3 \pm 8.1	t = 1.01 p = 0.31

1 - See text for definition.

2 - Means compared by t-test (variances equal in each case); RR = relative risk, C.I. = confidence interval.

* - Number of respondents; means \pm standard deviation.

Table 6

NEUROLOGIC EFFECT GROUPINGS

Ormet Aluminum

Hannibal, Ohio

HETA 84-426

June 25 - July 18, 1985

- Memory impairment:
- difficulty remembering things
 - observation by others of participant having difficulty remembering things
 - need to make notes to remember things
 - need to go back and check things such as turning off the stove or locking the door
- Cognitive dysfunction:
- difficulty concentrating
 - frequently confused or disoriented
 - difficulty getting the meaning from reading newspapers and books
 - difficulty thinking of the right words to make something clear to others
- Anxiety:
- palpitations of the heart (in the absence of physical exertion)
 - feeling of pressure in the chest
 - perspiring without any particular reason
- Neurasthenic symptoms:
- tire more easily than people of same age
 - frequently feel irritable for no particular reason
 - feel depressed for no particular reason
 - difficulty getting to sleep or staying asleep

Table 7

NEUROLOGIC EFFECTS AMONG POTROOM AND OTHER WORKERS

Ormet Aluminum
Hannibal, Ohio
HETA 84-426
June 25 - July 18, 1985

Effect*	<u>Potroom Department</u>		<u>All Others</u>	
	<u>Total</u>	<u>Number and (%) with effect</u>	<u>Total</u>	<u>Number and % with effect</u>
Memory impairment	314	141 (44.9)	326	179 (54.9)
Cognitive dysfunction	311	107 (34.4)	326	134 (41.1)
Anxiety	313	138 (44.1)	330	166 (50.3)
Neurasthenic symptoms	312	174 (55.8)	330	195 (59.1)

*See Table 6

Table 8

TIME IN POTROOM AND AGE OF PARTICIPANTS
ACCORDING TO PRESENCE OF NEUROLOGIC EFFECTS

Ormet Aluminum
Hannibal, Ohio
HETA 84-426
June 25 - July 18, 1985

Effect	Years in potroom		t-test ¹		Age (years) ²		t-test ¹	
	Effect	Effect	t	p	Effect	Effect	t	p
	present	absent			present	absent		
Memory impairment	7.3 (7.9), 309*	7.6 (8.2), 306	-0.35	0.73	40.8 (10.4), 306	40.2 (10.5), 305	-0.29	0.78
Cognitive dysfunction	7.0 (7.6), 235	7.7 (8.3), 379	-1.11	0.27	40.4 (10.5), 231	40.7 (10.5), 278	-1.01	0.32
Anxiety	7.4 (7.9), 295	7.5 (8.2), 325	-0.11	0.91	40.2 (9.8), 293	40.9 (11.1), 321	0.02	0.99
Neurasthenic symptoms	7.4 (7.8), 356	7.3 (8.3), 261	0.11	0.91	40.4 (9.7), 352	40.6 (11.3), 260	0.13	0.89

1. Variances equal in all cases

2. Age unknown for several participants

3. See Table 6

* Mean (standard deviation), number of participants